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THE ABSORPTION SPECTRA OF KRYPTON AND XENON IN THEIR REGIONS OF AUTOIONIZATION

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Laboratory Operations
THE AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
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LOS ANGELES AIR FORCE STATION
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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract F04701-72-C-0073.

The authors gratefully acknowledge the assistance of Mr. R. Marcoe in the laboratory and of Ms. E. Platz in the reduction of the data.

This report, which documents research carried out from November 1970 through November 1972, was submitted on 13 December 1972 to Lt Col Elliott W. Porter, DYX, for review and approval.

Approved

G. A. Paulikas, Director
Space Physics Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Elliott W. Porter, Lt Col, USAF
Executive Officer
Deputy for Technology

ABSTRACT

The absorption cross section spectra of krypton and xenon, obtained at narrow spectral bandwidths are reported. Both gases were studied in their regions of autoionization, 840 to 880 Å and 918 to 990 Å for Kr and Xe, respectively. In Kr over the entire wavelength range, and in Xe from 918 to 939.5 Å, the bandwidth employed was 0.04 Å. From 939.5 to 990 Å in Xe a bandwidth of 0.08 Å had to be used in order to avoid overlapping orders. Results are corrected for the integrating effect of the bandwidth where possible. More than twice as much structure than previously measured in the autoionizing series $^1S_o\,(4s)^2\,(4p)^6 \longrightarrow (4p)^5$ md' and $(4_p)^5$ ns' for Kr and $^1S_o\,(5s)^2\,(5p)^6 \longrightarrow (5p)^5$ md' and ns' for Xe is reported.

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FIGURES

Introduction

A valuable method of studying the physical properties of short-lived quasi-stationary atomic states is through the observation of their associated autoionization lines in photo-absorption. Observations of absorption structure in the rare gases at energies greater than the $^2P_{3/2}$ ionization threshold were first made by Cuthbertson[1] and Beutler[2]. Absorption cross sections have been measured between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization edges of krypton[3,4] and xenon[4-9] by a number of experimentalists. They have used either discrete line sources or a helium continuum source and a relatively broad band. The current multi-channel quantum defect theory and configuration interaction theory require data that can only be obtained with experimental apparatus having high spectral resolution. This laboratory has developed techniques for working in high resolution (0.04 Å) photoelectric absorption spectroscopy at wavelengths shorter than 1000 Å.[10] A logical utilization of this technique has been to obtain autoionization spectra of the rare gases in sufficient detail to delineate line profiles, transition intensities and energies.

Several years ago Hudson and Carter[10] studied the bandwidth dependence of their measured absorption cross sections in argon in the autoionization region from 776 to 788 Å. It became apparent that the bandwidth employed, which was a factor of 10 narrower than had been used in earlier work, resulted in a very significant increase in the amount of absorption structure which could be measured. In addition, a method was developed to correct the results for the integrating effect of the finite spectral bandwidth. For those lines whose widths were greater than the bandwidth (0.04 Å) it was possible to report cross sections which were no longer bandwidth dependent. This improved capability has been applied to the measurement of the absorption cross sections of krypton and xenon in their regions of autoionization; 840 to 880 Å and 918 to 990 Å, respectively.

Apparatus and Experimental Procedure

The absorption spectra were obtained using a 2.2-m McPherson scanning monochromator with a 1200 line/mm Bausch and Lomb grating blazed at 1500Å. Exit and entrance slits were set at $20 \pm 1\mu$. The krypton spectra, and the xenon spectra from 918.0 to 939.5Å were obtained in second order with a measured instrumental bandwidth of 0.04Å. At wavelengths longer than 939.5Å the xenon spectra were obtained in first order (0.08Å bandwidth). This was because third order absorption from wavelengths longer than 630Å interferred with second order measurements at wavelengths longer than 940Å. The light source was a repetitive discharge in helium, which gives rise to the Hopfield continuum. The absorbing gas was flowed into the main volume of the monochromator. The combination of differential pumping on the entrance slit, and a flexible bellows coupled to the exit slit which permitted separate detector-chamber pumping, allowed windowless operation over the range of absorption pressures employed. A more detailed description of the experimental apparatus is available in reference 10.

The absorption spectrum of each gas was recorded at 6 different pressures and consequently at 6 different atomic column numbers in the light path. Values of the column number ranged from 0.5×10^{16} particles/cm^2 to 2.4×10^{16} particles/cm^2. The minimum detectable cross section was therefore 2×10^{-18} cm^2. Cross sections at a given wavelength are obtained from the relationship

$$\frac{A_o(\lambda', \Delta\lambda)}{A(\lambda', \Delta\lambda)} = \exp N\bar{\sigma}(\lambda', \Delta\lambda)$$

where A_o and A are the levels of unabsorbed and transmitted light flux, λ' is the wavelength at the center of the bandwidth, $\Delta\lambda$ is the bandwidth, and N is the column number of absorbing atoms. The quantity $\bar{\sigma}$ $(\lambda', \Delta\lambda)$ is the value of the absorption cross section obtained following the instrumental integration of the true absorption cross section $\sigma(\lambda')$ across the finite bandwidth. The results of the study by Hudson and Carter[10] of the bandwidth dependence of measured uv absorption cross sections were used to adjust the peaks of the measured absorption lines upward and the minima between peaks downward.

Results

Figure 1 shows a plot of atomic absorption cross section versus wavelength for krypton. The column numbers of the absorbing gas were computed by normalizing to a value of 42×10^{-18} cm^2 for the cross section in the continuum at 845.6 Å reported by Metzger and Cook.[4] Their results at the peaks and minima of the observed structure are shown for comparison, as are the results of Huffman, et al.[3] Both these experimental efforts were conducted using a spectrographic bandwidth of 0.5 Å. As one would expect, their results tend to be higher at the minima and lower at the maxima then are detected with a 0.04 Å bandwidth system. Those peaks and minima which are corrected for the integrating effect of the bandwidth in the present work are indicated in the figure with an asterisk. The dashed portion of the curve has not been corrected because the structure at these wavelengths is equal to, or narrower than, the bandwidth. Had the present work been normalized to the result reported by Huffman, et al[7] in the continuum at 845.6 Å, our cross sections would be increased by approximately 25%.

The absorption curve shown in this figure was obtained by averaging the results from the six absorption runs. The standard deviation to the mean at a specific wavelength was never more than 2%. Wavelengths are accurate to within ± 0.08 Å which represents a considerable improvement over the wavelength accuracy of the earlier work which must be limited by the 0.5 Å bandwidth. The data shown here is in agreement with the earlier results at the two broadest peaks but shows a progressively greater discrepancy toward the shorter wavelength, narrower structure. The earlier work presents structure in which only three elements of the $(4p)^5$ ns' series are resolved and ten elements of the $(4p)^5$ md' series compared to nine and thirty elements, respectively, in the present work.

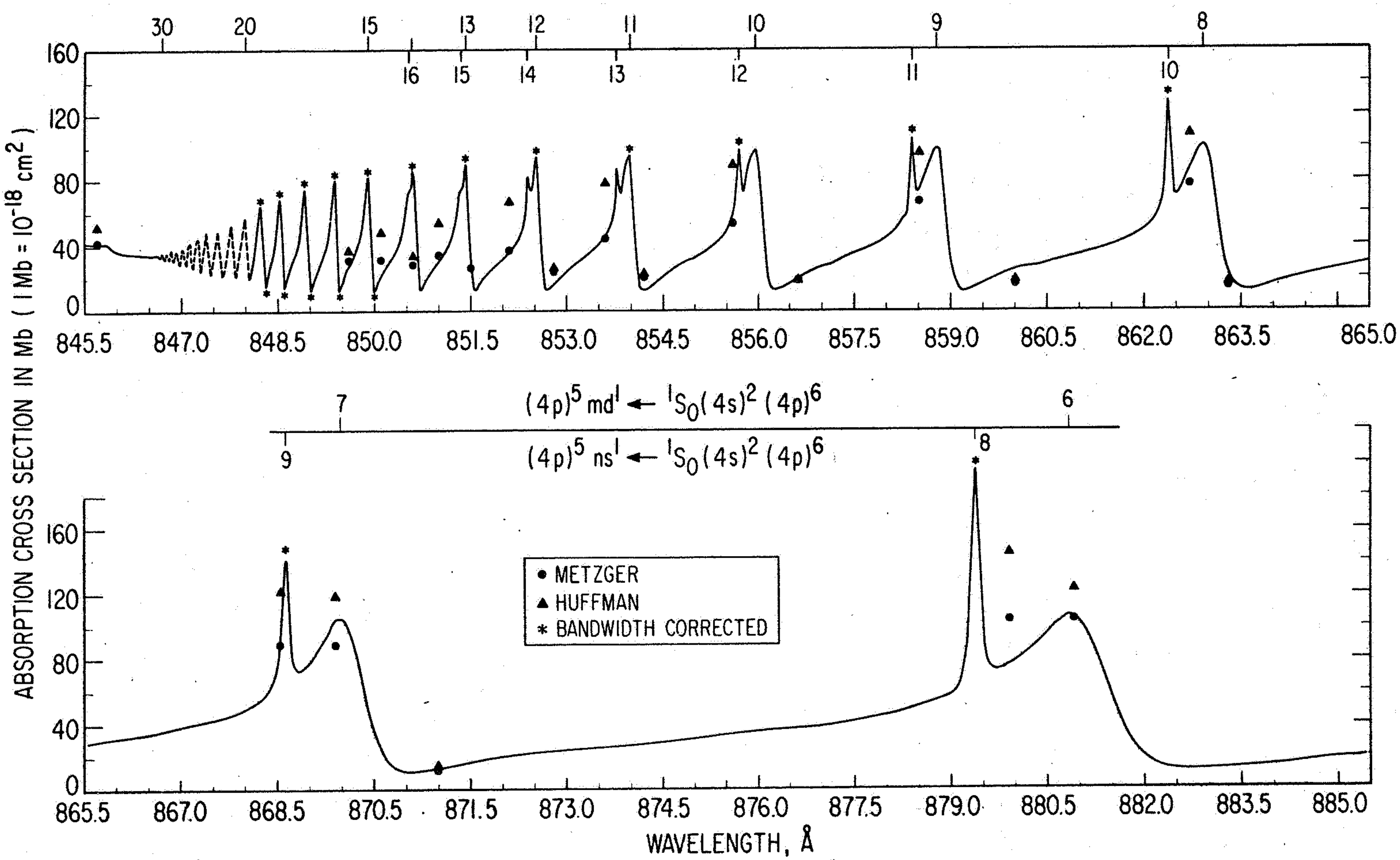

Fig. 1. The atomic-absorption cross section of krypton versus wavelength

Figure 2 shows a comparable set of absorption data for xenon in its autoionizing region. Again, results are normalized to the absorption cross section of 63.3×10^{-18} cm^2 in the continuum at 915 Å reported by Metzger and Cook.[4] Data reported by Huffman, et al[7], Samson,[8] Matsunaga, et al[9], and Metzger and Cook[4] are also shown for comparison. Had we normalized to the data of either Matsunaga, et al or Huffman, et al in the continuum, our results would be increased by either 10% or 24%, respectively. As in the previous figure, those maxima and minima in our work, which are corrected for bandwidth effects, are indicated with an asterisk. The structured interval at wavelengths shorter than 924.1 Å is dashed to show that no correction for bandwidth dependence has been attempted.

The results presented for xenon are the average of the 6 absorption runs with a standard deviation to the mean of less than 3% except in the vicinity of source emission lines. There are many emission lines in the helium source at those long wavelengths and a smooth fit across these intervals is presented. No attempt to estimate true peak heights of the ns' transitions was made. These narrow lines were difficult to superimpose from trace to trace in the computer solution for $\bar{\sigma}$. In addition, the lines gave indication of being number density (bandwidth) dependent, suggesting that the line width was less than the bandwidth, thus making a straightforward correction for bandwidth impossible. Agreement with Metzger and Cook[4] at 952 Å is excellent where the structure is broad and data from the first order spectrum is reported. This agreement deteriorates at the shorter wavelength narrower structure, both in magnitude and wavelength, just as in the case of krypton. At the transition of 966.7 Å (7d') the present work has yielded a result substantially lower than that of Metzger and Cook (102.5 compared to 137.7 Mb) but in relatively good agreement with the datum of Samson (90 Mb). It should be noted that at our normalization point of 915 Å Samson[8] (62 Mb) and Metzger and Cook[4] (63.3 Mb) essentially agree. This work in xenon extends the number of measured transitions from 12 to 25 in the $(5p)^5$ md' series and from 4 to 11 in the $(5p)^5$ ns' series.

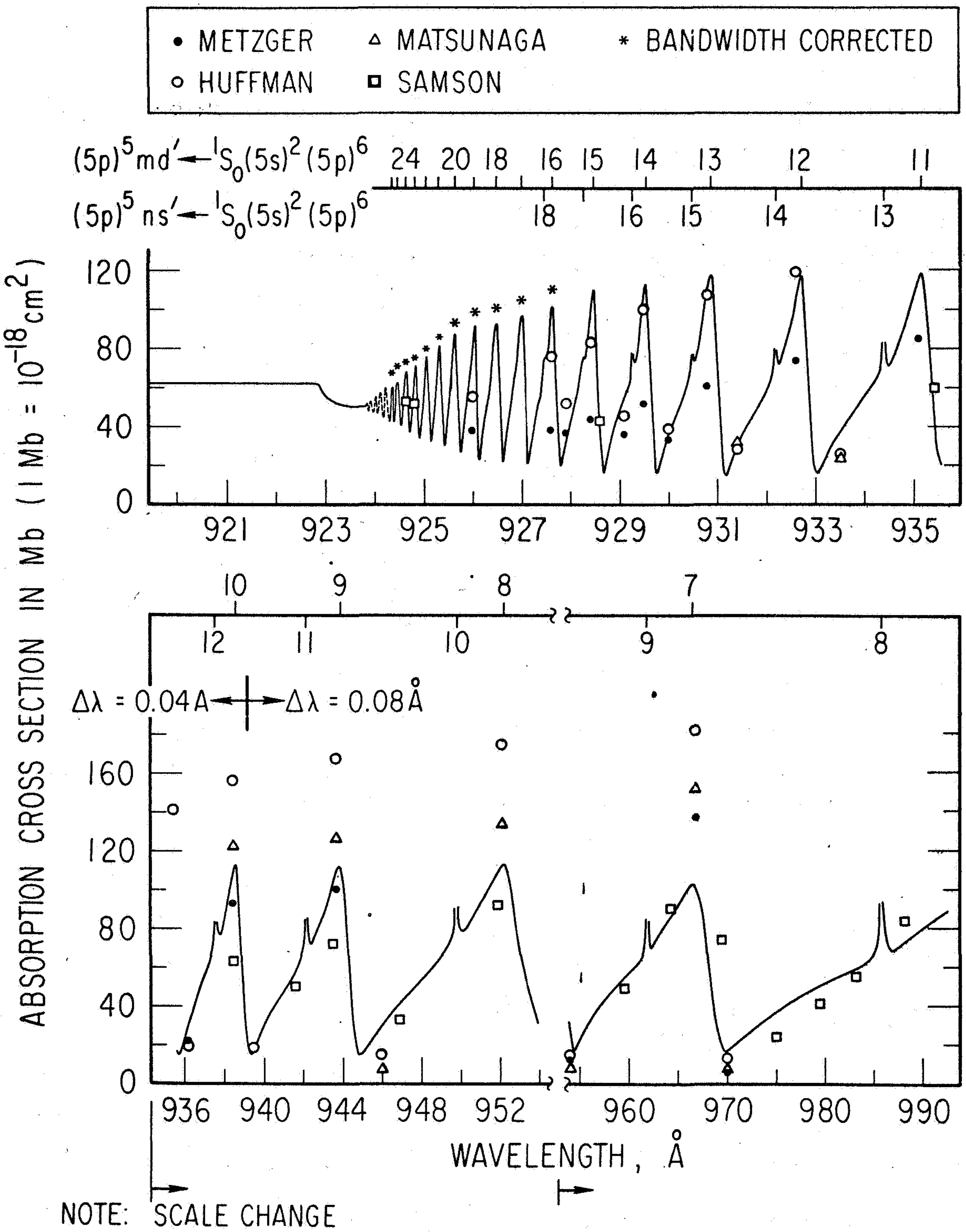

Fig. 2. The atomic-absorption cross section of xenon versus wavelength

Conclusions

The absorption cross section measurements reported for krypton and xenon represent a significant improvement in the available data; in the number of transitions measured, in their shape and relative accuracy, and in the location of the energies at which the transitions occur. It is hoped that the additional data reported here on krypton and xenon will encourage further theoretical work on the quasi-stationary states of the rare gases.

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